09/937851 PCT/SE 00/00597

REC'D 29 MAY 2000

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PATENT- OCH REGISTRERINGSVERKET

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Applicant (s)

(21) Patentansökningsnummer 9901137-1
Patent application number

(86) Ingivningsdatum 1999-03-29
Date of filing

Stockholm, 2000-05-22

För Patent- och registreringsverket
For the Patent- and Registration Office

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Avgift
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A PROCESS FOR STERILIZING A BIOLOGICALLY CONTAMINATED ENCLOSURE

The present invention relates to a process for sterilizing a biologically contaminated enclosure and particularly to a safe and easy chemical process for a well-controlled release or fumigation of formaldehyde gas from formalin. The process is intended for sterilizing biologically contaminated enclosures such as animal houses, hatcheries, feed stores, feed bins, feed tanks, feed mills, hospitals, medical instruments or other hard to reach areas in which the slowly and well controlled release of formaldehyde gas from easily available formalin solution is responsible for the complete sterilization by maximizing the excellent killing effects against bacteria, viruses and fungi.

BACKGROUND OF THE INVENTION

Discussion of related art

It is well known that formaldehyde gas is the mostly used gas in the sterilization of livestock buildings. It is an effective disinfectant against vegetative bacteria, fungi, spores and viruses if an adequate time of exposure and not less than 70% humidity are provided (Remington page 1171, Cooper & Mason 1964).

It can be easily absorbed by surfaces in both its gaseous or liquid state, as it has strong penetration power which increases in completely closed spaces.
In a study (Sykes, 1972) it was proved that formaldehyde can attain complete sterilization to a well closed room within two hours at 70% relative humidity.

Its mode of action on living cells is by reaction with the cellular protein and (DNA, RNA) amino acids (Russel, 1976).

Formalin, as a commercially available product, is an aqueous solution containing up to 37% by weight of formaldehyde, HCHO (30.03), with methanol added to prevent polymerization. The solution is extensively used for disinfecting rooms, which have been subjected to infection, by:

1. Reaction of formalin with half its weight of potassium permanganate.

2. Spraying it on sheets hung in the room.

3. Releasing formaldehyde vapor from formalin into the room by a heat generator or heater.

4. Subliming paraformaldehyde powder at 218°C using a heater.

All the above mentioned methods have many disadvantages. Using potassium permanganate to evaporate formaldehyde results in a very vigorous and dangerous reaction, which is completed within few seconds, and this does not give enough time for the worker to escape safely and many fatal accidents have been reported in real life.

It can be proved that spraying formalin on sheets is non-reproducible and does not release enough formaldehyde gas as it is temperature-dependent as can be seen from the following table

Concentration and type of formaldehyde	Time needed to kill spores	Time needed to kill bacteria
Formaldehyde gas	2 hours	2 hours
8% formalin	18 hours	18 hours
0.5% formalin	2-4 days	6-12 hours

Formaldehyde gas is thus described as being a sterilizing agent, while formalin (10% strength) is described as being an antiseptic agent; hence there is a need to use the formaldehyde gas as a sterilizer rather

than using the formalin, as formalin is time consuming and requires diligent application through decontamination. .
Reference: Remington's Pharmaceutical Sciences, 18th. Ed., pages 1171, 1470. Merck Index 11th Ed.

Further, contaminated, highly sophisticated electronic and dental equipment may be damaged by sterilizing liquid agents like those described in US Patent 31779 or by heat or autoclaving etc. US Patent 5552112 introduced a new method for sterilizing a metallic surgical instrument with microwave radiation but the method suffers from non-availability of microwave source to everyone and high cost. As mentioned in US Patent 5552112, gas sterilization with an ethylene oxide mixture is acceptable for both hanpieces and burs. However, this is impractical because of cost of equipment, long sterilization and aeration times involved, and cost of providing adequate protection for personnel. Alkaline glutaraldehyde (2%) as mentioned by Boucher in US Patent 3912450, is used to sterilize equipment, but it must be used for 10 hours to kill spore-forming organisms or tuberculosis microorganisms and is irritating to tissue.

Many workers could successfully release formaldehyde gas using generators or heaters and some patents have been published like US Patents: 4585624, 665794, 1837264, 2993832, 3694146, 3816074, 3898038 and 4166087. All these patents describe different apparatus systems for vaporizing formaldehyde and dispensing it into the enclosure to be sterilized for contact with contaminants. However, such methods suffer from high cost of instruments, maintenance, availability, complexity and restricted volume of formalin to be evaporated. No work has ever been known to use a safe chemical process for the evaporation of formaldehyde as an alternative for the unsafe usage of potassium permanganate or other conventional methods.

SUMMARY OF THE INVENTION

The present invention provides an ideal, chemical and safe process for releasing formaldehyde gas from a formalin solution by evaporation using heat generated by an exothermic reaction in order to simplify and optimize the use of formaldehyde gas in sterilizing closed spaces, like houses, buildings for housing animals, hospitals, operating rooms, stores, hotels, bath rooms or any object needing to be sterilized.

It is, therefore, an object of the present invention to provide a process for sterilizing enclosures, such as animal houses, hatcheries, feed stores, feed bins, feed tanks, feed hauling truck bins or tanks, feed mills or other hard to reach areas, or rooms in hospitals, clinics, research laboratories and the like by chemically releasing gaseous formaldehyde into the enclosure for contact with contaminants.

The present invention is based on the finding that the release of formaldehyde gas can be easily provided by heat generated by an exothermic reaction occurring in the presence of formalin. The released formaldehyde gas can be used for sterilizing closed spaces of the kind exemplified above. Exothermic chemical reactions involving various reagents are known to one skilled in the chemical art. In general, a chemist can chose any reagents for such exothermic reactions, and thus, the choice of reagents is not critical to the present invention. Needless to say, it is advantageous to chose reagents, which are easily available and cheep. Once chosen the amounts of reagents sufficient to generate heat for releasing gaseous formaldehyde for sterilization from formalin are easily determined by one skilled in the art. As a non-limiting example of appropriate reagents there can be mentioned amine compounds and peroxide compounds or precursors of peroxide compounds, which when mixed,

and in the presence of formalin, bring about an exothermic reaction releasing formaldehyde gas for sterilizing.

According to a preferred embodiment of the invention the exothermic reaction is provided by addition of reagents to the formalin in amounts sufficient to generate heat for releasing formaldehyde from the formalin. In accordance therewith, the reagents preferably comprise a mixture of a first reagent A and a second reagent B, said reagent A comprising an amine compound, optionally in admixture with sulphur sublime, red iron oxide, silica, preferably that sold under the tradename Aerosil, and citric acid, and the second reagent B comprising a peroxide compound, such as hydrogen peroxide, or a precursor thereof.

According to a most preferred embodiment, the reagent A comprises methenamine and the reagent B comprises a hydrogen peroxide solution. Mostly preferred, said solution contains 10-50% hydrogen peroxide.

In accordance with the present invention the formalin, for example having a concentration of 10-40% formaldehyde gas, is mixed with the reagent A, for example an amine compound, and the reagent B, for example hydrogen hydrogen peroxide. As explained below, the temperature of the reaction solution will increase spontaneously by the exothermic chemical reaction and the production of formaldehyde gas starts effectively at 60°C. The temperature rises and release of formaldehyde gas reaches the maximum value at 90°C.

As non-limiting examples of peroxide compounds the following can be mentioned: ammonium peroxosulfate, potassium peroxodisulfate, hydrogen peroxide, acetyl peroxide, benzoyl peroxide and cumene hydroperoxide. For the purpose of the present invention there are no specific limitations as to the choice of reagents.

According to a most preferred embodiment, wherein said reagents comprise an amine and hydrogen peroxide the ratio between these is within the range of 0.7-1.5.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention is illustrated by the following example:

To evaporate 10 ml up to maximum 3500 ml (preferably 2000 ml) of formalin containing 10%-40% of formaldehyde gas in water:

The above formalin quantity is mixed with 100gm-400gm, preferably 200 gm powder (A) which consists of five ingredients as follows:

Ingredient	Range in grams	Preferably in grams
Sulphur sublime	0-10	0.30
Iron oxide, red	0-10	0.30
"Aerosil"	0-5	0.40
Citric acid	0-5	4.00
Methenamine	180-210	195.00

In case of sterilizing highly sophisticated medical or dental instruments or other similar objects Methenamine (Hexamethyleneamine) without the rest of chemicals shown in the above table should be used.

After mixing the above quantity of powder (A) with the above amount of formalin, (100ml-400ml best results with 200ml) liquid (B) is added.

It is the powder part, which controls the reaction, and provides enough time for the operator before the onset of the evaporation process.

Liquid (B) is hydrogen peroxide having a concentration of 10%-50% (best results with 50%). It is the heat generated by mixing powder (A) and liquid (B) which helps in heating and evaporation or controlled fumigation of formalin.

After about five minutes, the temperature of the solution increases spontaneously by the exothermic chemical reaction and the production of formaldehyde gas starts effectively at 60° C. With the rise of the temperature of the exothermic reaction the evaporation of

formaldehyde gas becomes very strong and reaches the maximum at 90° C (after about 10 minutes).

EXAMPLE:

In order to illustrate the invention the following non-limiting example is given:

A 4000 m^3 (10000 bird capacity) chicken house was chosen to be sterilized immediately after the complete evacuation of the building and before the new bird cycle. The house was left as such without further cleaning. Swabs were taken from different representative areas of the house (ceiling, flour etc.). All windows and openings were tightly closed. The house was humidified with water to obtain at least 70% relative humidity. The chosen formalin amount for the experiment was 2 lit per $100m^3$, so 40 lit of (37%) formaldehyde solution were divided into 20 plastic containers (10 lit capacity each) such that each container contains 2 lit of formalin. The containers were placed evenly in the house. To each container 200 gm of powder (A) were added and consisting of:

Ingredient	Quantity (g)
Sulfur Sublime	0.30
Iron oxide, red	0.30
"Aerosil"	0.40
Citric acid	4.00
Methenamine	195.00
TOTAL	200.00

Powder (A) was mixed thoroughly with formalin and thereafter 200 ml of liquid (B) (50% hydrogen peroxide) were added to every container and mixed.

In every container solution temperatures were recorded against time, and the following average solution temperatures were obtained against time.

Time in minutes	Solution Temperature C
3	40
5	60
7	80
10	95
30	95
40	85
50	75
60	65
100	40

Formaldehyde started evaporating effectively when the temperature of the solution reached 60° C after 5 minutes of mixing all ingredients together.

After 10 minutes the evaporation became extensive (boiling).

This temperature was attained for 20 minutes before it declined and reached room temperature after two hours.

The chicken house was kept closed and empty for 48 hours after which it was well ventilated and swabs were taken again randomly and analyzed for total fungal and bacterial count.

Average count before sterilization	Average count after sterilization
1000,000 colonies/g	2 colonies/g

The present invention, therefore, is well suited and adapted to attain the intended objects and has the advantages and features mentioned as well as others inherent therein. The foregoing description is provided to illustrate the invention, and is not to be construed as a limitation. Numerous additions, substitutions and other changes can be made to the invention without departing from its scope as set forth in the appended claims.

CLAIMS

1. A process for sterilizing a biologically contaminated enclosure in which the enclosure is brought into contact with formaldehyde, c h a r a c t e r i z e d in that said formaldehyde is released from formalin by heat generated by an exothermic reaction occurring in the presence of said formalin.

2. A process of claim 1, wherein the exothermic reaction is provided by addition of reagents (A, B) to said formalin in amounts sufficient to generate heat for releasing formaldehyde from said formalin.

3. A process of claim 2, wherein said reagents comprise a mixture of a first reagent (A) and a second reagent (B), said reagent (A) comprising an amine compound, optionally in admixture with sulphur sublime, red iron oxide, silica and citric acid, and said second reagent (B) comprising a peroxide compound or a precursor thereof.

4. A process of claim 3, wherein said reagent (A) comprises methenamine and said reagent (B) comprises a hydrogen peroxide solution.

5. A process of any one of claims 2-4, wherein to evaporate formaldehyde gas from every 10 ml up to maximum 3500 ml of formalin the following ranges of constituents of reagent (A) are needed: (0-10) grams of sulphur sublime, (0-10) grams of red iron oxide, (0-5) grams of silica, (0-5) grams of citric acid and (180-210) grams of methenamine.

6. A process of claim 4, wherein the solution contains 10-50% hydrogen peroxide.

7. A process of any one of claims 2-6, wherein the ratio between the reagents (A, B) is 0.7-1.5.

8. A process of any one of claims 1-7, wherein the formalin has a concentration of 10-40% formaldehyde gas.

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SAMMANDRAG

Ett förfarande beskrivs för sterilisering av ett biologiskt förorenat utrymme, varvid utrymmet bringas i beröring med formaldehyd. Formaldehyden frisättes från formalin medelst värme, som alstras medelst en exoterm reaktion, som äger rum i närvaro av nämnda formalin.